

* 22.6	1	65.5	6	4103.4	3
27.0	3	81.1	4	07.9	7
34.2	6	83.3	2	09.2	5
43.9	5	86.0	2	20.8	6
48.6	6	* 99.1	6	22.6	8
* 58.3	5	3615.8	3	37.6	7
* 63.5	5	16.9	3	40.1	3
* 67.7	5	18.6	3	44.7	2
* 72.1	4	21.0	7	59.5	4
* 90.0	5	34.3	2	70.5	2
3132.9	8	37.7	6	* 85.3	2
34.6	8	38.5	6	* 96.6	0
35.7	6	47.8	3	*4208.6	1
36.7	9	61.6	7	* 64.0	3
39.2	9	68.1	6	* 81.6	4
42.4	5	70.1	6	4308.4	3
49.5	6	74.1	9	23.8	4
50.7	6	79.6	7	39.7	6
55.2	9	83.1	2	41.0	5
64.9	5	87.9	2	4359.6	5
70.1	7	3690.9	4	64.7	3
74.3	5	91.8	8	67.4	3
3246.9	10	3708.0	3		
53.9	10	13.9	3		

¹ Duffendack and Fox, *Nature*, 118, 12 (1926); *Science*, 64, 277 (1926); *Astrophys. J.*, in press.

² Barker and Duffendack, *Phys. Rev.*, 26, 339 (1925).

THE ENTROPY OF RADIATION

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The very close agreement between the formula of Planck and the measured distribution of black body radiation has led to numerous attempts to provide a theoretical basis for this formula. Of these the one receiving widest acceptance is that of Einstein,¹ who obtains the Planck formula by assuming merely that the chance of emission from an excited atom is increased by the presence of other light, of the same frequency as that which the atom emits, and that the increase is proportional to the concentration of that light.

I shall now approach this problem in a way which seems to me even more fundamental. The distribution of radiant energy in thermal equilibrium may be calculated as soon as we know the entropy of radiation as a function of concentration and of frequency. The notion of entropy may in turn

be referred to the still simpler notion of elementary probability. Without any premeditated attempt to obtain a particular result, I find that very simple assumptions regarding the probability lead directly to an expression for the entropy of radiation which is identical with the one obtained by Planck.

Adhering as closely as possible to the notation of Planck, the total radiant energy in a hollow (Hohlraum) will be designated by U , the energy density by $u = U/V$. The rate of change of energy density with frequency as we proceed through the spectrum will be called u_ν . Hence the density of energy lying between any two given frequencies is

$$\int_n^m u_\nu d\nu.$$

So also the total entropy, the entropy density, and the rate of change of entropy density with the frequency will be denoted by S , s , and s_ν . Planck makes the assumption that if the whole spectrum is divided into slices, each *slice* being that part of the radiation lying between two given frequencies, then the entropy of each slice, finite or infinitesimal, is the same as if that slice were alone in the hollow, all the remaining radiation being removed. I shall not go quite so far as this, but shall make a less sweeping assumption, the true significance of which will become apparent as we proceed. *Assumption I.* By taking successive intervals of frequency the whole radiation may be divided into slices so small that such quantities as u_ν and s_ν may be taken as constant throughout each slice, and yet so large that the entropy of each slice may be regarded as unchanged if all other radiation is removed.

As was first done by Joffé,² we may divide u_ν by $h\nu$ to obtain a new function $n_\nu = u_\nu/h\nu$, and from this obtain the related quantities, n and N . To anyone who has accepted the existence of light quanta or photons³ these new quantities N , n and n_ν will represent, respectively, the number of these particles, their concentration and the rate of change of this concentration with the frequency. Even those who have not accepted the existence of these particles as proved will permit us to use these terms in order to see the consequences that may follow from the employment of a method analogous to that employed in the study of the entropy of gases.

The problem that we have to solve is this: If we have a certain amount of radiation in a given enclosure, what is the change in entropy when this radiation is allowed to escape freely into a larger enclosure? This problem may be put in another way: Suppose that we have N particles in a large enclosure, what is the chance of finding at any instant that all of these particles are contained in a given portion of this enclosure?

If V' is the volume of the large enclosure, and V the smaller volume of the selected portion, and if there is only one particle present, the chance

that it will happen to be in the small volume is V/V' . Now if instead of one particle we have N particles, the simplest assumption is that the chance that any one particle will be in the volume V is independent of the number of other particles already there, in which case the chance that all the particles will be in the smaller volume is $(V/V')^N$, and applying the principle of Boltzmann, the difference in entropy between N particles in the volume V , and N particles in the volume V' is given by the expression

$$S - S' = k \ln (V/V')^N = kN \ln (V/V'). \quad (1)$$

This is the same as the expression for the change of entropy in the free expansion of a perfect gas. This equation for the dependence of the entropy of radiation upon the volume leads by known methods, which I shall not repeat here, to a formula for the distribution of radiant energy of the type of Wien's, which, as we know from experiment, is nearly but not quite in accordance with the truth. We also know that the corresponding expression for the entropy of a gas is not correct for any actual but only for an ideal gas.

We are, therefore, led to abandon the simplest assumption that the probabilities for the several particles are independent, and to try the following which is obviously the next simplest assumption. *Assumption II.* The chance of any one particle being in a selected volume V is a linear function of the number of particles already in that volume. Assumptions I and II suffice for a complete solution of the problem.

If then N particles are supposed to be enclosed in the fixed volume V' , the chance that they will all be in a selected portion of this volume V is $W = W_1 W_2 W_3 \dots W_N$, and the individual probability for any one particle, numbered $m + 1$, will be given by the equation,

$$W_{m+1} = \frac{V}{V'} + \frac{ma}{V'} \quad (2)$$

where V' and a are constants. If we had been dealing with the molecules of a gas which have no effect on one another, except that each has a finite volume, we should find this same equation, in which the constant a would have a negative value. In our present case we shall regard a as completely undetermined as to sign and magnitude.

The probability that all N particles will be in the volume V is, therefore,

$$W = \frac{V}{V'} \frac{V+a}{V'} \dots \frac{V+(N-1)a}{V'} = \left(\frac{a}{V'}\right)^N \left[\frac{V}{a} \left(\frac{V}{a} + 1\right) \dots \left(\frac{V}{a} + N - 1\right) \right]. \quad (3)$$

Our problem is not changed if, keeping V' , V and N in the same ratios, we make them as large as we please. We may, therefore, make V/a very large and, without loss of generality, an integer, so that

$$W = \left(\frac{a}{V'}\right)^N \frac{\left(\frac{V}{a} + N - 1\right)!}{\left(\frac{V}{a} - 1\right)!} \quad (4)$$

Now from the Boltzmann equation for the difference in entropy of N molecules in V and N molecules in V' ,

$$S - S' = k \ln W, \quad (5)$$

and we may employ the Stirling formula, neglecting those terms which become rapidly negligible when V/a and N become very large, in the form

$$\ln x! = x \ln x - x \quad (6)$$

and also neglecting unity in comparison with V/a and N , we find

$$S - S' = kN \ln \frac{a}{V'} + k \left(\frac{V}{a} + N\right) \ln \left(\frac{V}{a} + N\right) - k \frac{V}{a} \ln \frac{V}{a} - kN. \quad (7)$$

The quantity a has less effect upon the expression of entropy, the larger the volume is; as we may consider that V' was originally taken so large compared with V that the entropy S' is in the region of validity of equation (1). Hence, we may write

$$S' = kN \ln \frac{V'}{Nb}, \quad (8)$$

where Nb is a constant analogous to an integration constant, and may for the present be regarded as undetermined.

Combining (7) and (8), and performing a mere algebraic rearrangement, we find

$$S = kN \ln \frac{a}{be} + \frac{kV}{a} \left[\left(1 + \frac{Na}{V}\right) \ln \left(1 + \frac{Na}{V}\right) - \frac{Na}{V} \ln \frac{Na}{V} \right], \quad (9)$$

where e is the base of the natural logarithms. Dividing by the volume, we obtain the expression for the entropy density as a function of the concentration, $n = N/V$,

$$s = kn \ln \frac{a}{be} + \frac{k}{a} [(1 + na) \ln (1 + na) - na \ln na]. \quad (10)$$

So far it has not been necessary to be particular as to the kind of radiation present in the hollow or as to whether the correction factor a is the same when the particles are all of nearly the same frequency or of quite different frequencies. But now, in order to inspect more closely the meaning of this correction factor we may consider that we have present in the hollow only one of our slices of radiation, lying between the fre-

quencies ν and $\nu + \Delta\nu$. Then by Assumption I, $s_\nu = s/\Delta\nu$ and $n_\nu = n/\Delta\nu$, and equation (10) becomes

$$s_\nu = kn_\nu \ln \frac{a}{be} + \frac{k}{a\Delta\nu} [(1 + n_\nu a \Delta\nu) \ln (1 + n_\nu a \Delta\nu) - n_\nu a \Delta\nu \ln n_\nu a \Delta\nu]. \quad (11)$$

We may now introduce the thermodynamic principle embodied in Wien's displacement law. From any of the familiar expressions for that law we may readily obtain the equation,

$$s_\nu = n_\nu f\left(\frac{n_\nu}{\nu^2}\right) \text{ or } s_\nu = \nu^2 F\left(\frac{n_\nu}{\nu^2}\right). \quad (12)$$

Hence by inspection of any one of the terms of (11) we see that $n_\nu a \Delta\nu$ is a function only of n_ν/ν^2 , and, therefore, a is proportional to $1/\nu^2 \Delta\nu$. The factor of proportionality is now an absolute constant independent of any of the variables which determine the state of the system. It will, however, depend upon the units in which these variables are expressed, but this dependence may also be eliminated if we note that a has the dimensions of (length),³ while $1/\nu^2 \Delta\nu$ has the dimensions of (time).³ Introducing c , the velocity of light, we have

$$a = \frac{\alpha c^3}{\nu^2 \Delta\nu}, \quad (13)$$

where α is now independent of the variables and the units. It is, therefore, a pure number. We also see by inspection, comparing equations (11) and (12), that b must depend upon the variables in the same way as a , and, therefore, if β is another pure number,

$$b = \frac{\beta c^3}{\nu^2 \Delta\nu}. \quad (14)$$

Equation (11) now becomes

$$s_\nu = kn_\nu \ln \frac{\alpha}{\beta e} + \frac{k\nu^2}{\alpha c^3} \left[\left(1 + \frac{n_\nu \alpha c^3}{\nu^2}\right) \ln \left(1 + \frac{n_\nu \alpha c^3}{\nu^2}\right) - \frac{n_\nu \alpha c^3}{\nu^2} \ln \frac{n_\nu \alpha c^3}{\nu^2} \right]. \quad (15)$$

While we have thus acquired information regarding the quantity a by purely mathematical methods, it will be interesting to translate this information into physical terms. Assumption I states that the entropy of one slice of radiation is independent of the presence of other slices. Therefore, any statement regarding the probability that the particles of a given slice be in a certain volume cannot be affected by the presence or absence of particles belonging to other slices. On the other hand, it can-

not be assumed that the particles are affected only by other particles of precisely the same frequency, for presumably no two particles have frequencies which are exactly the same. We are thus forced to regard the mutual effect of two particles as a sort of resonance phenomenon, diminishing with great rapidity as the difference in frequency between the two particles increases. (It seems probable that this mutual effect would almost entirely disappear with a difference of frequency as great as the width of a fine spectral line.)

Since we are about to find that a is positive, we might be tempted to regard this mutual effect of two particles as analogous to attraction. Indeed, I was formerly tempted to assume an average diminution in the velocity of a particle in the presence of other like particles; or, in other words, that the refractive index of a space containing radiation is slightly higher than unity. It is, perhaps, possible that such a phenomenon may be found if we ever are able to study radiation of enormous density, such as exists in the interior of the stars. But I am now convinced that it is entirely negligible in the region of our present measurements. If there were such a change in the velocity of radiation in the presence of other radiation, most of our thermodynamics of radiation, including the Stefan-Boltzmann law and Wien's displacement law, would fall to the ground.

I feel that the mutual effect of one particle upon the probability of the presence of another particle is a more subtle thing than can be accounted for by the mere assumption of forces acting between the particles *after they have started* from emitting atom to absorbing atom. But this is a matter which I cannot discuss further here, but must postpone until I have developed further my new theory of light.⁴

Returning to equation 15, we may substitute $u_\nu = h\nu n_\nu$, and find

$$s_\nu = \frac{ku_\nu}{h\nu} \ln \frac{\alpha}{\beta e} + \frac{k\nu^2}{\alpha c^3} \left[\left(1 + \frac{\alpha c^3 u_\nu}{h\nu^3} \right) \ln \left(1 + \frac{\alpha c^3 u_\nu}{h\nu^3} \right) - \frac{\alpha c^3 u_\nu}{h\nu^3} \ln \frac{\alpha c^3 u_\nu}{h\nu^3} \right]. \quad (16)$$

This is the equation obtained by Planck if we assume that

$$\alpha = \frac{1}{8\pi}. \quad (17)$$

This assumption completes the definition of the interesting quantity a . To obtain precisely the Planck form it would be necessary to assume also that $\alpha = \beta e$. This assumption, however, is unimportant and probably unnecessary. It affects only the additive term in the entropy equation, and, as we shall see in a further development of the subject, there is no inconvenience in leaving β undetermined for the present.

It is interesting to note that not a but $a \Delta \nu$ is specific, or, in other words independent of the width of the slice considered. If we now substitute the new value of α and write

$$\frac{a \Delta \nu}{c} = \frac{c^2}{8 \pi \nu^2}, \quad (18)$$

we have a quantity which is of the dimensions of an area. Now there have been several attempts to calculate what, for brevity, has been called the cross-section of the quantum,⁵ and the one by Dr. Smith and myself, based on a classical formula of Lord Rayleigh, gave just this expression $c^2/8 \pi \nu^2$. I do not wish to stress this point here, but merely allude to it in passing.

Finally, it may be pointed out that, owing to the peculiar phrasing of Assumption I, we have obtained the Planck equation for entropy not as an exact formula but as an approximation; but certainly, admitting the general validity of the methods here employed, it follows that if equation 1 represents the first approximation to the law of entropy, equation (16) represents the obvious and necessary second approximation.

¹ Einstein, *Physik. Z.*, **18**, 121 (1917).

² Joffé, *Ann. Physik*, **36**, 534 (1911).

³ Lewis, *Nature*, **118**, 874 (1926).

⁴ Lewis, these PROCEEDINGS, **12**, 22 (1926).

⁵ Ornstein and Burger, *Zs. Physik*, **20**, 345 (1924); Lewis and Smith, *J. Amer. Chem. Soc.*, **47**, 1508 (1925).

LINEAR ELEMENTS OF THE ELECTROMAGNETIC PINHOLE GRAPHS*

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Following the suggestion at the end of the last paper¹ a new adjustment of apparatus was chosen, in which the condenser, C (Fig. 1), is charged directly on open circuit. Here B is the spring break (conveniently kept in resonance with the lighting circuit in the key of B), E and R electromotive force (2 cells) and resistance, T , p , telephone and organ pipe, I , II , primary and secondary of the transformer. When B is open, C is charged by E and discharged on closing. The coils I and II were eventually to be removed. The pinhole probe bc has its point about 1 cm. from the bottom of the pipe p .

Figure 2 shows the s , C graphs for the intervals 0 to 1.1 m.f. These